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Invention: COMPOSITION FOR ANTIREFLECTION COATING AND METHOD FOR FORMING PATTERN



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# PATENT ABSTRACTS OF JAPAN

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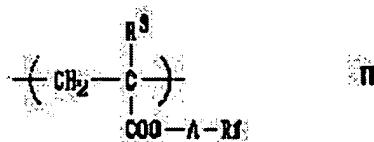
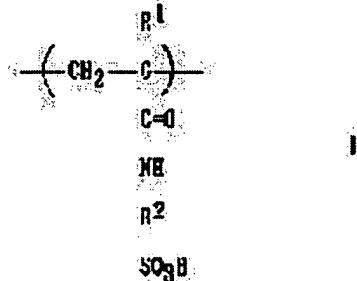
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## (54) BASE-INTERCEPTING ANTIREFLECTION FILM AND RESIST PATTERN FORMING METHOD

### (57)Abstract:

PURPOSE: To improve resolution, developability, pattern formation and the efficiency of application by containing a specified copolymer and/or salt, and fluoroalkyl sulfonic acid and/or fluoroalkyl carboxylic acid.

CONSTITUTION: A base-intercepting antireflection film contains a copolymer having one kind of a repeat unit expressed by the formula I and one kind of a repeat unit expressed by the formula II and/or fluoroalkyl sulfonic acid having a fluoroalkyl group with the carbon number of 5-15 and/or fluoroalkyl carboxylic acid having a fluoroalkyl group with the carbon number of 5-15. In the formula I, R<sub>1</sub> indicates a hydrogen atom or an organic group, and R<sub>2</sub> indicates a bivalent organic group. In the formula II, R<sub>3</sub> indicates a hydrogen atom or an organic group, R<sub>f</sub> indicates a fluoroalkyl group, and A indicates direct coupled alkylene group or a fluoroalkylene group. Thus, in the lithography process, the influence of a basic material in the atmosphere can be completely intercepted, and a standing-wave effect can be reduced enough.



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## CLAIMS

## [Claim(s)]

[Claim 1] (b) The copolymer which has at least one sort of repeating units expressed with at least one sort of repeating units expressed with the following type (1), and the following type (2), and/or its salt, The base cutoff nature antireflection film characterized by the fluoro alkyl sulfonic acid and/or carbon number in which a (b) carbon number has the fluoro alkyl group of 5-15 containing the fluoro alkyl carboxylic acid which has the fluoro alkyl group of 5-15.

## [Formula 1]



In [type (1)], R1 shows a hydrogen atom or an organic radical, and R2 shows a divalent organic radical. ]

## [Formula 2]



In [type (2)], R3 shows a hydrogen atom or an organic radical, Rf shows a fluoro alkyl group, and A shows direct coupling, an alkylene group, or a fluoro alkylene group. ]

[Claim 2] The formation approach of the resist pattern which in forming a resist pattern by applying a resist, forming a resist coat on a substrate, irradiating a radiation in a predetermined pattern configuration at this resist coat, and subsequently developing negatives is beforehand characterized by irradiating a radiation after forming the base cutoff nature antireflection film according to claim 1 on said resist coat.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the formation approach of the resist pattern using the base cutoff nature antireflection film useful to micro processing by the lithography process which uses the resist which induces various kinds of radiations, especially a chemistry magnification mold resist, and this base cutoff nature antireflection film.

[0002]

[Description of the Prior Art] In the field of micro processing represented by manufacture of an integrated circuit device, in order to obtain the higher degree of integration of an integrated circuit, detailed-ization of the processing size in a lithography process is progressing, and development of the lithography process which is stabilized and can perform micro processing of high degree of accuracy with a line breadth of 0.5 micrometers or less is strongly furthered in recent years. However, by the approach using a conventional visible ray (wavelength of 800-400nm) and a conventional near ultraviolet ray (wavelength of 400-300nm), the depth of focus with broader difficult therefore forming such a detailed pattern in high degree of accuracy can be attained, and the lithography process using the radiation of short wavelength (wavelength of 300nm or less) effective in detailed-izing of a design rule is proposed. As a lithography process using the radiation of such short wavelength, it is KrF. The approach of using charged-particle lines, such as far ultraviolet rays, such as an excimer laser (wavelength of 248nm) and an ArF excimer laser (wavelength of 193nm), and X-rays, such as a synchrotron radiation line, or an electron ray, is proposed. And as a high resolution resist corresponding to the radiation of such short wavelength, the so-called "chemistry magnification mold resist" attracts attention, and amelioration and development of current and this chemistry magnification mold resist serve as an important technical theme in a lithography process. A chemistry magnification mold resist makes the compound (henceforth an "acid generator") which generates an acid by the exposure of the radiation contained in it generate an acid by irradiating a radiation (henceforth "exposure"). By the catalysis of this acid In a resist coat, chemical reactions (for example, a polar change, cleavage of a chemical bond, crosslinking reaction, etc.) are made to occur, and the solubility over a developer forms a pattern using the phenomenon of changing in the exposure section. About such a chemistry magnification mold resist The alkali compatibility radical in alkali fusibility resin Combination of the resin and the acid generator which protected by t-butyl ester group or the t-butoxycarbonyl group (for example, refer to JP,59-45439,A); The combination of the resin and the acid generator which protected the alkali compatibility radical in alkali fusibility resin by the silyl radical ; Others [ combination / (for example, refer to JP,2-25850,A) / of acetal radical content resin and an acid generator ], (For example, refer to JP,60-52845,A) Combination of alkali fusibility resin, a dissolution control agent, and an acid generator; much proposals, such as combination of novolak resin, a cross linking agent, and an acid generator, are made.

[0003] However, a chemistry magnification mold resist tends to be influenced of the moisture which exists in the ambient atmosphere in a lithography process, oxygen, an alkali, etc., and has a problem in

respect of process stability. For example, the dimethylaniline of the minute amount contained in an ambient atmosphere carries out deactivation of the acid near a front face among the acids generated in the resist coat by exposure, a refractory-sized layer is formed in this resist coat front face, and remaining in the shape of eaves on the surface of a resist pattern, after this refractory-sized layer's developing negatives is reported to SPIE, Vol.1466, "Advance in Resist Technologyand Processing", and p.2 (1991, A.MacDonald et al.). Such a refractory-sized layer not only reduces the sensibility and resolving power of a resist, but the eaves produced in the resist pattern have an adverse effect on a subsequent etching precision. And although the magnitude of these eaves tends to increase with the increment in the neglect time amount which intervenes between each of a series of process of the BEKU-development after exposure-exposure, this phenomenon is called postexposure time delay (henceforth "PED"), and has become the factor which reduces remarkably the admissibility on the time amount in a lithography process. As an approach of solving the problem about such PED, on a chemistry magnification mold resist coat Carrying out the laminating of the protective coat which intercepts a coat front face from an ambient atmosphere is proposed. To WO 92/No. 05474 Protective coats, such as polyacrylic acid, a polyvinyl butyral, polyvinyl alcohol, and polystyrene sulfonate, by carrying out a laminating on a chemistry magnification mold resist coat Encroachment of the alkali to the inside of a resist coat is controlled, and preventing the sensibility of a resist and lowering of resolution is indicated. However, it cannot say that they can not necessarily prevent effectively formation of a refractory-sized layer which was mentioned above among such protective coats while polyacrylic acid, a polyvinyl butyral, and polyvinyl alcohol have a barrier operation, and acidity of polystyrene sulfonate is too strong and it is a fault to make the chemical reaction by the catalysis of the acid in a chemistry magnification mold resist start irrespective of the existence of exposure. Furthermore, although these protective coats are generally applied on a resist coat as a water solution, they cannot say that wettability with the resist coat of the water solution is enough, but also have the fault of being easy to produce spreading unevenness.

[0004] On the other hand, the radiation usually used for a lithography process Since it is single wavelength, even if the phenomenon which an incidence radiation and the radiation reflected by the vertical interface of a resist coat interfere mutually within a resist coat, consequently is called the "standing wave effectiveness" or "multiplex cross protection", i.e., light exposure, is fixed If the thickness of a resist coat is changed, by interference between radiations in the film, the phenomenon of changing the effectual light exposure to a resist coat arises, and it may have an adverse effect on formation of a resist pattern. since [ for example, ] spreading thickness changes with the slight differences among the presentation of a resist, viscosity, the spreading conditions of a resist, etc. or a level difference is in a substrate -- the difference of spreading thickness -- being generated (the direction of a crevice becoming thicker than heights) -- according to the difference of those thickness, the effectual light exposure to a resist coat changes, a pattern dimension is changed or the dimensional accuracy of a resist pattern falls. In order to solve the problem about such standing wave effectiveness, the antireflection film is formed on a resist coat, the echo by the resist coat interface is suppressed, and the method of reducing multiplex interference within the film is proposed. for example, J.Electrochem.Soc., Vol.137, and No. -- carrying out the laminating of a polysiloxane, poly ethyl vinyl ether, the polyvinyl alcohol, etc. as antireflection film, and making 12 and 3900 (1990) reduce the standing wave effectiveness on a resist coat is indicated. In this case, depending on the refractive index and thickness of the antireflection film, the refractive index of the ideal antireflection film of the reflective depressor effect in a resist coat interface is mainly rootn ( $n$  is the refractive index of a resist), and it is supposed that they are the thickness of the ideal antireflection film odd lambda/4m (lambda is the wavelength of a radiation and m is the refractive index of the antireflection film) times. However, since the difference of a refractive index with a resist is small, there is a fundamental problem that the standing wave effectiveness cannot be controlled enough in the antireflection film which consists of a polysiloxane, poly ethyl vinyl ether, or polyvinyl alcohol. Moreover, like a polysiloxane, with an antireflection film insoluble to water or a developer, solubility [ further as opposed to / the process separately remove by the antireflection film remover is needed, and / water or a developer by the case of poly ethyl vinyl ether or polyvinyl alcohol ] cannot necessarily say that it is enough in front of

development, but residue remains on a resist coat or there is a fault -- resist engine performance, such as resolution, and development nature, a pattern configuration, may get worse. Moreover, like poly ethyl vinyl ether or polyvinyl alcohol, when applied on a resist coat as a water solution, the fault of being easy to produce spreading unevenness rather than enough also has wettability with the resist coat of a water solution.

[0005]

[Problem(s) to be Solved by the Invention] Then, in the lithography process which produces the integrated circuit of a high degree of integration using a resist, while the object of this invention can intercept the effect of the alkali in an ambient atmosphere thoroughly Can reduce the standing wave effectiveness enough and, moreover, it excels in the solubility over water and a developer. Also in case a special remover except water or a developer is not needed and it applies as a solution, wettability with a resist coat is good and is to offer the new base cutoff nature antireflection film excellent also in spreading nature. Other objects of this invention can solve simultaneously formation of the refractory-ized layer of a chemistry magnification mold resist coat front face, and the effect by the standing wave effectiveness, and are to offer the formation approach of a resist pattern of moreover having excelled in resolution, development nature, a pattern configuration, spreading nature, etc.

[0006]

[Means for Solving the Problem] according to this invention -- said technical problem -- the 1st (\*\*) -- it has at least one sort of repeating units expressed with at least one sort of repeating units expressed with the following type (1), and the following formula (2) -- a copolymer (It is hereafter called "a copolymer (I -1)".) And/or, the salt (it is hereafter called "a copolymer salt (I -2)".) (\*\*) -- the fluoro alkyl sulfonic acid (it is hereafter called "a fluoro alkyl sulfonic acid (low 1)".) with which a carbon number has the fluoro alkyl group of 5-15 and/or, the base cutoff nature antireflection film characterized by a carbon number containing the fluoro alkyl carboxylic acid (henceforth "a fluoro alkyl carboxylic acid (low 2)" which has the fluoro alkyl group of 5-15 -- be alike is attained.

[0007]

[Formula 1]

[0008] In [type (1), R1 shows a hydrogen atom or an organic radical, and R2 shows a divalent organic radical. ]

[0009]

[Formula 2]

[0010] In [type (2), R3 shows a hydrogen atom or an organic radical, Rf shows a fluoro alkyl group, and A shows direct coupling, an alkylene group, or a fluoro alkylene group. ]

[0011] Moreover, therefore, it is attained by the formation approach of the resist pattern which in forming a resist pattern when according to this invention said technical problem applies a resist, forms a resist coat on a substrate the 2nd, is exposed in a predetermined pattern configuration and subsequently develops negatives on this resist coat is characterized by exposing after forming said base cutoff nature antireflection film on said resist coat beforehand.

[0012] Hereafter, although this invention is explained to a detail, thereby, the object, the configuration, and effectiveness of this invention will become clear.

The copolymer (I -1) which constitutes a copolymer (I -1) and the base cutoff nature antireflection film of copolymer salt (I -2) this invention For example, at least one sort of sulfonic group content partial saturation monomers corresponding to the repeating unit expressed with a formula (1) (it is hereafter called a "sulfonic group content monomer".) At least one sort of fluoro alkyl group content partial saturation monomers corresponding to the repeating unit expressed with a formula (2) (it is hereafter called a "fluoro alkyl group content monomer".) It can manufacture by copolymerizing the monomer mixture to contain.

[0013] In a formula (1), although R1 shows a hydrogen atom or an organic radical and R2 shows a divalent organic radical, a straight chain or branched chain is sufficient as these organic radicals. As an organic radical of R1, the organic radical of carbon numbers 1-12 is desirable. As the example A methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, An isobutyl radical, sec-butyl, t-

butyl, n-pentyl radical, alkyl group [ of the carbon numbers 1-12, such as n-hexyl group, ]; -- carboxyl group; -- a carboxymethyl radical -- 2-carboxy ethyl group, 2-carboxy propyl group, 3-carboxy propyl group, The carboxy alkyl group of the carbon numbers 2-12, such as 2-carboxy butyl, 3-carboxy butyl, and 4-carboxy butyl; A methoxycarbonyl group, An ethoxycarbonyl radical, an n-propoxy carbonyl group, an isopropoxycarbonyl radical, The alkoxy carbonyl group of the carbon numbers 2-12, such as n-butoxycarbonyl radical and t-butoxycarbonyl; An acetoxy radical, The acyloxy radical of the carbon numbers 2-12, such as a propionyloxy radical, butanoyloxy, and a benzoyloxy radical; A phenyl group, The aryl group of the carbon numbers 6-12, such as a KUMENIRU radical; The aralkyl radical; methoxy group of the carbon numbers 7-12, such as benzyl and alpha-methylbenzyl radical, An ethoxy radical, n-propoxy group, an isopropoxy group, an n-butoxy radical, The alkoxy group of the carbon numbers 1-12, such as t-BUCHITOKISHI radical; A methoxymethyl radical, An ethoxy methyl group, 2-methoxy ethyl group, 2-ethoxyethyl radical, 2-methoxy propyl group, 3-methoxy propyl group, 2-methoxy butyl, The alkoxyalkyl group of the carbon numbers 2-12, such as 3-methoxy butyl and 4-methoxy butyl; A cyclopentylic group, The cycloalkyl radical of the carbon numbers 3-12, such as a cyclohexyl radical, a cycloheptyl radical, and a cyclo octyl radical; a cyano group, the radical guided from these organic radicals can be mentioned.

[0014] As a divalent organic radical of R2, the divalent organic radical of carbon numbers 1-12 is desirable. Moreover, as the example A methylene group, ethylene, 1, 2-propylene radical, 1, 3-propylene radical, 1 and 1-dimethyl ethylene, the 1-methyl -1, 3-propylene radical, 1, 4-butylene radical, the 1-methyl -1, 4-butylene radical, the 2-methyl -1, 4-butylene radical, 1, 5-pentene radical, 1, and 1-dimethyl -1, 4-butylene radical, 2, and 2-dimethyl -1, 4-butylene radical, 1, 2-dimethyl -1, 4-butylene radical, 1, and 6-hexylene radical etc. can be mentioned. 1 and 1-dimethyl ethylene is especially desirable among these divalent organic radicals.

[0015] As an example of such a sulfonic group content monomer A 2-(meta) acrylamide-isobutane sulfonic acid, a 2-alpha-carboxy acrylamide-isobutane sulfonic acid, A 2-alpha-carboxymethyl acrylamide-isobutane sulfonic acid, A 2-alpha-methoxycarbonyl acrylamide-isobutane sulfonic acid, A 2-alpha-acetoxy acrylamide-isobutane sulfonic acid, A 2-alpha-phenyl acrylamide-isobutane sulfonic acid, A 2-alpha-benzyl acrylamide-isobutane sulfonic acid, A 2-alpha-methoxy acrylamide-isobutane sulfonic acid, A 2-alpha-(2-methoxy ethyl) acrylamide-isobutane sulfonic acid, a 2-alpha-cyclohexyl acrylamide-isobutane sulfonic acid, a 2-alpha-cyano acrylamide-isobutane sulfonic acid, etc. can be mentioned. These sulfonic group content monomers are independent, or two or more sorts can be mixed and used for them. In this invention, a 2-(meta) acrylamide-isobutane sulfonic acid is desirable especially as a sulfonic group content monomer.

[0016] Next, in a formula (2), although R3 shows a hydrogen atom or an organic radical, Rf shows a fluoro alkyl group and A shows direct coupling, an alkylene group, or a fluoro alkylene group, a straight chain or branched chain is sufficient as the organic radical of R3. A hydro fluoro alkyl group or a perfluoroalkyl radical is sufficient as the fluoro alkyl group of Rf, and a straight chain or branched chain is sufficient as it. Furthermore, a hydro fluoro alkylene group or a perfluoro alkylene group is sufficient as the fluoro alkylene group of A, and a straight chain or branched chain is sufficient as it.

[0017] As an organic radical of R3, the organic radical of carbon numbers 1-12 can mention the organic radical of the carbon numbers 1-12 desirable and same as the example as R1 in a formula (1).

[0018] As a fluoro alkyl group of Rf, the fluoro alkyl group of carbon numbers 1-15 is desirable. As the example Difluoromethyl group, a perfluoro methyl group; A 2 and 2-difluoro ethyl group, 2, 2, and 2-trifluoro ethyl group, a perfluoro ethyl group; 1-(perfluoro methyl) ethyl group, 2-(perfluoro methyl) ethyl group, 2, 2 and 3, 3-tetrafluoro propyl group, A perfluoro ethyl methyl group, a JI (perfluoro methyl) methyl group, Perfluoro propyl group; 1-methyl - 2, 2, 3, and 3-tetrafluoro propyl group, 1-(perfluoro ethyl) ethyl group, 2-(perfluoro ethyl) ethyl group, 2, 2, 3, 3, 4, and 4-hexafluoro butyl, 2, 2, 3, 4 and 4, 4-hexafluoro butyl, A perfluoro propylmethyl radical, perfluoro butyl; 1 and 1-dimethyl - 2, 2, 3, and 3-tetrafluoro propyl group, 1 and 1-dimethyl - 2, 2, 3, 3, and 3-pentafluoro propyl group, 1-methyl - 2, 2, 3, 3, 4, and 4-hexafluoro butyl, 1-(perfluoro propyl) ethyl group, 2-(perfluoro propyl) ethyl group, 2, 2, 3, 3, 4, 4 and 5, 5-octafluoropentyl radical, A perfluoro butyl methyl group, a perfluoro

pentyl radical; 1 and 1-dimethyl - 2, 2, 3, 3, 4, and 4-hexafluoro butyl, 1 and 1-dimethyl - 2, 2, 3, 3, 4, 4, and 4-heptafluoro butyl, 1-methyl - 2, 2, 3, 3, 4, 4, 5, and 5-octafluoropentyl radical, 1-(perfluoro butyl) ethyl group, 2-(perfluoro butyl) ethyl group, 2, 2, 3, 3, 4, 4, 5, 5, 6, and 6-deca fluoro hexyl group, A perfluoro pentyl methyl group, a perfluoro hexyl group; 1 and 1-dimethyl - 2, 2, 3, 3, 4, 4, 5, and 5-octafluoropentyl radical, 1 and 1-dimethyl - 2, 2, 3, 3, 4, 4, 5, 5, and 5-nona fluoro pentyl radical, 1-methyl - 2, 2, 3, 3, 4, 4, 5, 5, 6, and 6-deca fluoro hexyl group, 1-(perfluoro pentyl) ethyl group, 2-(perfluoro pentyl) ethyl group, A 2, 2, 3, 3, 4, 4, 5, 5, 6, 6, 7, and 7-dodeca fluoro heptyl radical, A perfluoro hexyl methyl group, a perfluoro heptyl radical; 1-(perfluoro hexyl) ethyl group, A 2-(perfluoro hexyl) ethyl group, 2, 2, 3, 3, 4, 4, 5, 5, 6, 6, 7, 7 and 8, and 8-tetra-deca fluoro octyl radical, A perfluoro heptyl methyl group, a perfluoro heptyl methyl group, a perfluoro octyl radical; 1-(perfluoro heptyl) ethyl group, 2-(perfluoro heptyl) ethyl group, 2, 2, 3, 3, 4, 4, 5, 5, 6, 6, 7, 7, 8, 8 and 9, and 9-hexa deca fluoro nonyl radical, A perfluoro octyl methyl group, a perfluoro nonyl radical; 1-(perfluoro octyl) ethyl group, 2-(perfluoro octyl) ethyl group, 2, 2, 3, 3, 4, 4, 5, 5, 6, 6, 7, 7, 8, 8, 9, 9 and 10, and 10-OKUTA deca fluoro decyl group, a perfluoro nonyl methyl group, a perfluoro decyl group, etc. can be mentioned.

[0019] Moreover, as an alkylene group of A, the alkylene group of carbon numbers 1-5 is desirable, and can mention methylene group, ethylene, 1, 2-propylene radical, 1, 3-propylene radical, 1, and 1-dimethyl ethylene, 1-methyl - 1, 3-propylene radical, 1, and 4-butylene radical etc. as the example. As a fluoro alkylene group of A, the fluoro alkylene group of carbon numbers 1-5 is desirable. As the example Perfluoro methylene group, 1, and 1-difluoro ethylene, perfluoro ethylene, 1 and 1-difluoro - 1, 2-propylene radical, 2, 2 and 3, 3-tetrafluoro - 1, 3-propylene radical, The perfluoro - 1, 3-propylene radical, 1, and 1-dimethyl - 2, 2-difluoro ethylene, 1-methyl - 2, 2, 3, and 3-tetrafluoro - 1, 3-propylene radical, 2, 2, 3, 3 and 4, 4-hexafluoro - 1, 4-butylene radical, perfluoro - 1, 4-butylene radical, etc. can be mentioned.

[0020] As an example of such a fluoro alkyl group content monomer Difluoromethyl (meta) acrylate, perfluoro methyl (meta) acrylate; 2 and 2-difluoro ethyl (meta) acrylate, 2, 2, and 2-trifluoro ethyl (meta) acrylate, perfluoro ethyl (meta) acrylate; 1-(perfluoro methyl) ethyl (meta) acrylate, 2-(perfluoro methyl) ethyl (meta) acrylate, 2, 2 and 3, 3-tetrafluoro propyl (meta) acrylate, Perfluoro ethyl methyl (meta) acrylate, JI (perfluoro methyl) methyl (meta) acrylate, Perfluoro propyl (meta) acrylate; 1-methyl - 2, 2, 3, and 3-tetrafluoro propyl (meta) acrylate, 1-(perfluoro ethyl) ethyl (meta) acrylate, 2-(perfluoro ethyl) ethyl (meta) acrylate, 2, 2, 3, 3, 4, and 4-hexafluoro butyl (meta) acrylate, Perfluoro propylmethyl (meta) acrylate, perfluoro butyl (meta) acrylate; 1 and 1-dimethyl - 2, 2, 3, and 3-tetrafluoro propyl (meta) acrylate, 1 and 1-dimethyl - 2, 2, 3, 3, and 3-pentafluoro propyl (meta) acrylate, 2-(perfluoro propyl) ethyl (meta) acrylate, 2, 2, 3, 3, 4, 4 and 5, 5-octafluoropentyl (meta) acrylate radical, Perfluoro butyl methyl (meta) acrylate, perfluoro pentyl (meta) acrylate; 1 and 1-dimethyl - 2, 2, 3, 3, 4, and 4-hexafluoro butyl (meta) acrylate, 1 and 1-dimethyl - 2, 2, 3, 3, 4, 4, and 4-heptafluoro butyl (meta) acrylate, 2-(perfluoro butyl) ethyl (meta) acrylate, 2, 2, 3, 3, 4, 4, 5, 5 and 6, and 6-deca fluoro hexyl (meta) acrylate, Perfluoro pentyl methyl (meta) acrylate, perfluoro hexyl methyl (meta) acrylate; 1 and 1-dimethyl - 2, 2, 3, 3, 4, 4, 5, and 5-octafluoropentyl (meta) acrylate, 1 and 1-dimethyl - 2, 2, 3, 3, 4, 4, 5, 5, and 5-nona fluoro pentyl (meta) acrylate, 2-(perfluoro pentyl) ethyl (meta) acrylate, 2, 2, 3, 3, 4, 4, 5, 5, 6 and 7, and 7-dodeca fluoro heptyl (meta) acrylate, Perfluoro hexyl methyl (meta) acrylate, perfluoro heptyl (meta) acrylate; 2-(perfluoro hexyl) ethyl (meta) acrylate, 2, 2, 3, 3, 4, 4, 5, 5, 6, 6, 7, 7, 8, and 8-tetra-deca fluoro octyl (meta) acrylate, Perfluoro heptyl methyl (meta) acrylate, perfluoro octyl (meta) acrylate; 2-(perfluoro heptyl) ethyl (meta) acrylate, 2, 2, 3, 3, 4, 4, 5, 5, 6, 6, 7, 7, 8, 8, 9, 9, 10, and 10-OKUTA deca fluoro DESHIRU (meta) acrylate, [0021] besides the fluoro alkyl (meta) acrylate whose carbon numbers of a fluoro alkyl group, such as perfluoro nonyl methyl (meta) acrylate and perfluoro DESHIRU (meta) acrylate, are 1-20 alpha-carboxy acrylate, (2, 2, and 2-trifluoro ethyl) alpha-carboxy acrylate, (2, 2, and 2-trifluoro ethyl) alpha-carboxymethyl acrylate, (Perfluoro ethyl methyl) alpha-carboxymethyl acrylate; (2, 2, and 2-trifluoro ethyl) alpha-methoxycarbonyl acrylate, (Perfluoro ethyl

methyl) alpha-methoxycarbonyl acrylate; (2, 2, and 2-trifluoro ethyl) alpha-acetyloxy acrylate, (Perfluoro ethyl methyl) alpha-acetyloxy acrylate; (2, 2, and 2-trifluoro ethyl) alpha-phenyl acrylate, (Perfluoro ethyl methyl) alpha-phenyl acrylate; (2, 2, and 2-trifluoro ethyl) alpha-benzyl acrylate, (Perfluoro ethyl methyl) alpha-benzyl acrylate; (2, 2, and 2-trifluoro ethyl) alpha-ethoxy acrylate, (Perfluoro ethyl methyl) alpha-ethoxy acrylate; (2, 2, and 2-trifluoro ethyl) alpha-2-methoxy ethyl acrylate, (Perfluoro ethyl methyl) alpha-2-methoxy ethyl acrylate; (2, 2, and 2-trifluoro ethyl) alpha-cyclohexyl acrylate, (Perfluoro ethyl methyl) alpha-cyclohexyl acrylate; (2, 2, and 2-trifluoro ethyl) (Perfluoro ethyl methyl) alpha-cyanoacrylate, alpha(perfluoro ethyl methyl)-cyanoacrylate, etc. can be mentioned. These fluoro alkyl group content monomers are independent, or two or more sorts can be mixed and used for them.

[0022] In this invention, as a fluoro alkyl group content monomer, the fluoro alkyl (meta) acrylate whose carbon numbers of a fluoro alkyl group are 1-20 is desirable, and especially the fluoro alkyl (meta) acrylate that perfluoroalkyl (meta) acrylate and a perfluoroalkyl radical combined with the ester oxygen atom through a methylene group or ethylene especially is desirable.

[0023] a copolymer (I -1) -- setting -- the copolymerization rate of a sulfonic group content monomer and a fluoro alkyl group content monomer -- the total quantity of both monomers -- being based -- a sulfonic group content monomer -- usually -- 1 - 99 % of the weight -- desirable -- 3 - 50 % of the weight -- especially -- desirable -- 5 - 30 % of the weight -- it is -- moreover, a fluoro alkyl group content monomer -- usually -- it is 95 - 70 % of the weight especially preferably 97 to 50% of the weight preferably 99 to 1% of the weight. In this case, when a fluoro alkyl group content monomer exceeds [ the amount of the sulfonic group content monomer used ] 99 % of the weight at less than 1 % of the weight, there is an inclination for the solubility over the water or the developer of a base cutoff nature antireflection film to fall, and for a pattern configuration and development nature to fall, and the amount of the sulfonic group content monomer used exceeds 99 % of the weight, at less than 1 % of the weight, reduction of the standing wave effectiveness as an antireflection film serves as [ a fluoro alkyl group content monomer ] imperfection, or there is an inclination for membrane formation nature to fall.

[0024] In this invention, copolymerization of a sulfonic group content monomer and a fluoro alkyl group content monomer, and these monomers and other comonomers which can be copolymerized can be carried out. The amount of other comonomers used in this case is usually 40 or less % of the weight preferably 50 or less % of the weight based on all monomers.

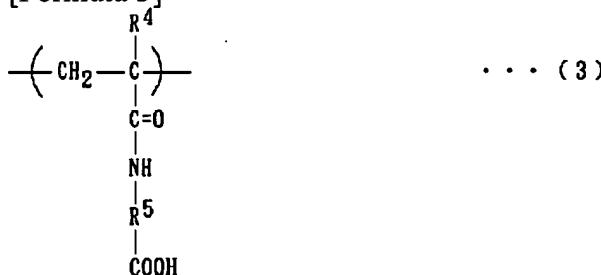
[0025] As such other comonomers, for example (meta) An acrylic acid, a crotonic acid, A cinnamic acid, an atropic acid, 3-acetyloxy (meta) acrylic acid, a 3-benzyloxy (meta) acrylic acid, Partial saturation monocarboxylic acid system compounds, such as alpha-methoxy acrylic acid and 3-cyclohexyl (meta) acrylic acid; Methyl (meta) acrylate, Ethyl (meta) acrylate, n-propyl (meta) acrylate, Alkyl (meta) acrylate system compounds, such as n-butyl (meta) acrylate, Partial saturation monocarboxylic acid ester system compounds, such as crotonic-acid methyl and methyl cinnamate; A fumaric acid, Partial saturation polycarboxylic acid system compounds, such as a maleic acid, a citraconic acid, mesaconic acid, and an itaconic acid; Monod or G methyl ester of said partial saturation polycarboxylic acid, Monod or G ethyl ester, Monod, Monod, such as G n-propyl ester, or a G ester system compound; Vinyl acetate, Unsaturated alcohol ester system compounds, such as propionic-acid vinyl and caproic-acid vinyl; (meta) Acrylonitrile, alpha-methylacrylonitrile, alpha-chloro acrylonitrile, alpha-chloro methylacrylonitrile, Vinylcyanide system compounds, such as alpha-trifluoromethyl acrylonitrile and cyanidation vinylidene; Styrene, Aromatic series mono-vinyl system compounds other than [ said ] alpha methyl styrene, vinyltoluene, etc.; A vinyl chloride, Vinylidene-chloride and vinyl fluoride, vinylidene fluoride, tetrafluoroethylene, Halogenation olefinic compounds, such as hexafluoropropylene; A butadiene, An isoprene, a chloroprene, piperylene, 2, 3-dimethylbutadiene, Methyl pentadiene, a cyclopentadiene, a vinyl cyclohexene, Diene series, such as ethylidene norbornene, a divinylbenzene, and a dimethyl vinyl styryl silane; The methyl vinyl ether, Partial saturation ether system compounds, such as ethyl vinyl ether and the methyl allyl compound ether; Glycidyl (meta) acrylate, Epoxy group content unsaturated compounds, such as allyl glycidyl ether; 2-chloro ethyl vinyl ether, Halogen content unsaturated-compound;2-hydroxyethyl (meta) acrylate other than [ said ]

chloroacetic-acid vinyl, a chloroacetic-acid allyl compound, chloro methyl styrene, etc., 2-hydroxypropyl (meta) acrylate, hydroxystyrene, Hydroxyl-group content unsaturated compounds, such as N-methylol (meta) acrylamide, 2-propenyl alcohol, and 2-methyl-2-propenyl alcohol; (meta) amide group content unsaturated compounds other than [ said ] acrylamide, a crotonic-acid amide, a cinnamic-acid amide, etc.;

[0026] Carboxyl group content unsaturated compounds other than [ said ] 2-(meta) acryloyloxyethyl succinic acid, 2-(meta) acryloyloxyethyl phthalic acid, 2-(meta) acryloyloxyethylhexahydrophthalic acid, 2-(meta) acryloyloxyethyl maleic acid, the carboxyl group content acrylamide system compound expressed with the following type (3) etc. can be mentioned.

[0027]

[Formula 3]



[0028] In [type (3), R4 shows a hydrogen atom or an organic radical, and R5 shows a divalent organic radical. ] As an organic radical of R4, the organic radical of the same carbon numbers 1-12 as R1 in said formula (1) can be mentioned, and the divalent organic radical of the same carbon numbers 1-12 as R2 in said formula (1) can be mentioned as a divalent organic radical of R5, for example.

[0029] As an example of said carboxyl group content acrylamide system compound A 2-(meta) acrylamide-isobutane carboxylic acid, a 2-alpha-carboxy acrylamide-isobutane carboxylic acid, A 2-alpha-carboxymethyl acrylamide-isobutane carboxylic acid, A 2-alpha-methoxycarbonyl acrylamide-isobutane carboxylic acid, A 2-alpha-acetoxy acrylamide-isobutane carboxylic acid, A 2-alpha-phenyl acrylamide-isobutane carboxylic acid, A 2-alpha-benzyl acrylamide-isobutane carboxylic acid, A 2-alpha-methoxy acrylamide-isobutane carboxylic acid, A 2-alpha-(2-methoxy ethyl) acrylamide-isobutane carboxylic acid, a 2-alpha-cyclohexyl acrylamide-isobutane carboxylic acid, a 2-alpha-cyano acrylamide-isobutane carboxylic acid, etc. can be mentioned. Other comonomers of these are independent, or can mix and use two or more sorts. In this invention, said carboxyl group content acrylamide system compound, especially a 2-(meta) acrylamide-isobutane carboxylic acid are desirable as other comonomers in said alkyl (meta) acrylate system compound especially methyl (meta) acrylate, and an ethyl (meta) acrylate; list.

[0030] Copolymerization for manufacturing a copolymer (I -1) can be manufactured with various polymerization gestalten, such as a bulk polymerization, a suspension polymerization, a massive-suspension polymerization, an emulsion polymerization, solution polymerization, and a precipitation polymerization, by proper approaches, such as a radical polymerization, anionic polymerization, cationic polymerization, and coordination polymerization. these copolymerization -- facing -- reaction components, such as each monomer and a polymerization initiator, -- at once -- the whole quantity -- or it has divided -- it is -- it can add continuously. Moreover, a copolymer (I -1) can also be manufactured by the chemical after treatment of a suitable precursive copolymer by the case.

[0031] Next, as for a copolymer salt (I -2), some sulfonic groups [ at least ] of a copolymer (I -1) are neutralized. A copolymer salt (I -2) for example, some sulfonic groups [ at least ] of the sulfonic group content monomer in the (i) copolymer (I -1) the approach of neutralizing with an alkaline compound, and (ii) -- with other comonomers by the case, after an alkaline compound neutralizes some sulfonic groups [ at least ] of a sulfonic group content monomer beforehand [ monomer / fluoro alkyl group content ] For example, it can manufacture by the approach of copolymerizing like the case where a copolymer (I -1) is manufactured etc. In the approach of the above (i), when acidic groups other than the

sulfonic group of a sulfonic group content monomer exist, this acidic group may also be neutralized. In the approach of the above (ii), the copolymerization rate of a sulfonic group content monomer and a fluoro alkyl group content monomer is still the same as that of the case of a copolymer (I -1), and when other comonomers used by the case have an acidic group, this a part of acidic group [ at least ] can also be neutralized. It sets to this invention and, as for a copolymer salt (I -2), it is desirable to add and mix and to manufacture a copolymer (I -1) in the water solution of an alkaline compound, by the approach of the above (i).

[0032] In this invention, it is desirable to use ammonia and/or an organic amine as an alkaline compound used in case a copolymer salt (I -2) is manufactured. As said organic amine, for example Monomethylamine, ethylamine, propylamine, A butylamine, dimethylamine, diethylamine, a dipropyl amine, Dibutyl amine, a trimethylamine, triethylamine, tripropylamine, Tributylamine, ethanolamine, aminomethyl propanol, 2-dimethylethanolamine, diethanolamine, triethanolamine, Cyclohexylamine, a pyrrole, a pyrrolidine, oxazole, a pyridine, first class [, such as a piperidine and a morpholine, ] - univalent amines; and ethylenediamine of the third class -- first class [, such as diethylenediamine, tetraethylenediamine, diethylenetriamine, tetra-ethylene triamine, an imidazole, imidazolidine, oxazole, pyrazine, a piperazine, and s-triazine, ] - the multiple-valued amines of the third class can be mentioned. The third class organic amine of univalent or many \*\* is desirable among these organic amines. Said organic amine is independent, or two or more sorts can be mixed and used for it. In this invention, ammonia and the univalent third class organic amine are desirable especially as an alkaline compound. whenever [ neutralization / of the copolymer salt (I -2) in this invention ] -- the sulfonic group of the sulfonic group content monomer -- usually -- 5-100-mol % -- it is 30-90-mol % preferably.

[0033] A copolymer (I -1) and a copolymer salt (I -2) can take various structures, such as a random copolymer, a block copolymer, and a graft copolymer. Even if a sulfonic group content monomer and a fluoro alkyl group content monomer live together during the same polymer block in the case of a block copolymer, you may exist during a different polymer block, and, in the case of a graft copolymer, both sulfonic group content monomer and fluoro alkyl group content monomer can live together in a trunk polymer and/or a branch polymer further, and either the trunk polymer or the branch polymer may be clitteringly constituted only for the sulfonic group content monomer.

[0034] In this invention a desirable copolymer (I -1) or a desirable copolymer salt (I -2) (a) 2-(meta) acrylamide-isobutane sulfonic acid, In a list, The copolymer of the fluoro alkyl (meta) acrylate whose carbon numbers of a fluoro alkyl group are 1-20 (salt); A (b)2-(meta) acrylamide-isobutane sulfonic acid, The carbon number of a fluoro alkyl group is a copolymer (salt) with the fluoro alkyl (meta) acrylate which are 1-20, and said alkyl (meta) acrylate system compound as other comonomers and/or said carboxyl group content acrylamide system compound.

[0035] Especially a desirable copolymer (salt) among the above (a) or the copolymer (salt) of (b) (c) 2-(meta) acrylamide-isobutane sulfonic acid, Perfluoroalkyl (meta) acrylate and a perfluoroalkyl radical mind a methylene group or ethylene. In a list, The copolymer of the fluoro alkyl (meta) acrylate chosen from the group of the fluoro alkyl (meta) acrylate combined with the ester oxygen atom (salt); A (d)2-(meta) acrylamide-isobutane sulfonic acid, The fluoro alkyl (meta) acrylate chosen from the group of the fluoro alkyl (meta) acrylate which perfluoroalkyl (meta) acrylate and a perfluoroalkyl radical combined with the ester oxygen atom through a methylene group or ethylene It is a copolymer (salt) with said alkyl (meta) acrylate system compound and/or said carboxyl group content acrylamide system compound. When the especially desirable copolymer (I -1) in this invention and a copolymer salt (I -2) are shown more concretely, the copolymer (salt) of the group of the above (c) A 2-(meta) acrylamide-isobutane sulfonic acid, (c-1) The copolymer of perfluoroalkyl (meta) acrylate (salt); (c-2) A 2-(meta) acrylamide-isobutane sulfonic acid, The copolymer (salt); (c-3) 2-(meta) acrylamide-isobutane sulfonic acid of the fluoro alkyl (meta) acrylate which the perfluoroalkyl radical combined with the ester oxygen atom through the methylene group, Copolymer (salt); and (c-4) the 2-(meta) acrylamide-isobutane sulfonic acid of the fluoro alkyl (meta) acrylate which the perfluoroalkyl radical combined with the ester oxygen atom through ethylene, Perfluoroalkyl (meta) acrylate and a perfluoroalkyl radical mind a methylene group. A copolymer with the mixture of the fluoro alkyl (meta) acrylate combined with the

ester oxygen atom (salt); (c-5) A 2-(meta) acrylamide-isobutane sulfonic acid, Perfluoroalkyl (meta) acrylate and a perfluoroalkyl radical mind ethylene. A copolymer with the mixture of the fluoro alkyl (meta) acrylate combined with the ester oxygen atom (salt); (c-6) A 2-(meta) acrylamide-isobutane sulfonic acid, The fluoro alkyl (meta) acrylate and the perfluoroalkyl radical which the perfluoroalkyl radical combined with the ester oxygen atom through the methylene group mind ethylene. In a list (c-7), A copolymer with the mixture of the fluoro alkyl (meta) acrylate combined with the ester oxygen atom (salt); A 2-(meta) acrylamide-isobutane sulfonic acid, Perfluoroalkyl (meta) acrylate The fluoro alkyl (meta) acrylate and the perfluoroalkyl radical which the perfluoroalkyl radical combined with the ester oxygen atom through the methylene group mind ethylene. It is a copolymer (salt) with the mixture of the fluoro alkyl (meta) acrylate combined with the ester oxygen atom, and is [0036]. Moreover, the copolymer (salt) of the group of the above (d) and a 2-(meta) acrylamide-isobutane sulfonic acid, (d-1) A copolymer (salt); (d-2) 2-(meta) acrylamide-isobutane sulfonic acid with perfluoroalkyl (meta) acrylate, and said alkyl (meta) acrylate system compound and/or said carboxyl group content acrylamide system compound, The fluoro alkyl (meta) acrylate which the perfluoroalkyl radical combined with the ester oxygen atom through the methylene group A copolymer with said alkyl (meta) acrylate system compound and/or said carboxyl group content acrylamide system compound (salt); (d-3) A 2-(meta) acrylamide-isobutane sulfonic acid, The fluoro alkyl (meta) acrylate which the perfluoroalkyl radical combined with the ester oxygen atom through ethylene A copolymer with said alkyl (meta) acrylate system compound and/or said carboxyl group content acrylamide system compound (salt); (d-4) A 2-(meta) acrylamide-isobutane sulfonic acid, The mixture of the fluoro alkyl (meta) acrylate which perfluoroalkyl (meta) acrylate and a perfluoroalkyl radical combined with the ester oxygen atom through the methylene group, A copolymer with said alkyl (meta) acrylate system compound and/or said carboxyl group content acrylamide system compound (salt); (d-5) A 2-(meta) acrylamide-isobutane sulfonic acid, The mixture of the fluoro alkyl (meta) acrylate which perfluoroalkyl (meta) acrylate and a perfluoroalkyl radical combined with the ester oxygen atom through ethylene, A copolymer with said alkyl (meta) acrylate system compound and/or said carboxyl group content acrylamide system compound (salt); (d-6) A 2-(meta) acrylamide-isobutane sulfonic acid, The mixture of the fluoro alkyl (meta) acrylate which the fluoro alkyl (meta) acrylate and the perfluoroalkyl radical which the perfluoroalkyl radical combined with the ester oxygen atom through the methylene group combined with the ester oxygen atom through ethylene, In a list (d-7), A copolymer with said alkyl (meta) acrylate system compound and/or said carboxyl group content acrylamide system compound (salt); A 2-(meta) acrylamide-isobutane sulfonic acid, Perfluoroalkyl (meta) acrylate The mixture of the fluoro alkyl (meta) acrylate which the fluoro alkyl (meta) acrylate and the perfluoroalkyl radical which the perfluoroalkyl radical combined with the ester oxygen atom through the methylene group combined with the ester oxygen atom through ethylene, and before It is a copolymer (salt) with an account alkyl (meta) acrylate system compound and/or said carboxyl group content acrylamide system compound. [0037] A copolymer (I - 1) and a copolymer salt (I - 2) can also be hydrogenated and used when a carbon-carbon unsaturated bond exists. The rate of hydrogenation in this case is 90% or less, and is usually 50% or less especially preferably 70% or less preferably.

[0038] the polystyrene equivalent weight average molecular weight (henceforth "Mw") of a copolymer (I - 1) and a copolymer salt (I - 2) -- usually -- 1,000-1,000,000 -- it is -- desirable -- 1,500-500,000 -- it is 2,000-100,000 especially preferably. When the inclination for the spreading nature at the time of Mw of a copolymer (I - 1) and a copolymer salt (I - 2) forming a base cutoff nature antireflection film less than by 1,000, membrane formation nature, etc. to fall is shown and 1,000,000 is exceeded, the inclination for the solubility over water or a developer, spreading nature, etc. to fall is shown. In this invention, a copolymer (I - 1) and a copolymer salt (I - 2) are independent respectively, or can mix and use two or more sorts.

[0039] As for a fluoro alkyl sulfonic acid (low 1) and a fluoro alkyl carboxylic acid (low 2) next the fluoro alkyl sulfonic acid (low 1) that constitutes the base cutoff nature antireflection film of this invention, and a fluoro alkyl carboxylic acid (low 2), a carbon number has the fluoro alkyl group of 5-15. A hydro fluoro alkyl group or a perfluoroalkyl radical is sufficient as this fluoro alkyl group, and a

straight chain or branched chain is sufficient as it. Others [ alkyl group / of the carbon numbers 5-15 illustrated for example about Rf of a formula (2) as said fluoro alkyl group / fluoro ], 1, 1, 2, 2, 3, 3, 4, 4, 5, 5-deca fluoro pentyl radical; 1, 1, 2, 2, 3, 3, 4, 4, 5, 5 and 6, a 6-dodeca fluoro hexyl group; 1, 1, 2, 2, 3, 3, 4, 4, 5, 5, 6, 6, 7, and 7-tetra-deca fluoro heptyl radical;

**\* NOTICES \***

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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**DESCRIPTION OF DRAWINGS**

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**[Brief Description of the Drawings]**

[Drawing 1] It is drawing showing the decision criterion of the cross-section configuration of a pattern, and each pattern configuration.

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[Translation done.]